Atomically Dispersed Ru-doped Ti\textsubscript{4}O\textsubscript{7} Electro catalysts for Chlorine Evolution Reaction with a Universal Activity

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Chlorine has been supplied by the chlor-alkali process that deploys dimensionally stable anodes (DSAs) for the electrochemical chlorine evolution reaction (CIER). The paramount bottlenecks have been ascribed to an intensive usage of precious elements and inevitable competition with the oxygen evolution reaction. Herein, a unique case of Ru\textsuperscript{2+}-O\textsubscript{4} active motifs anchored on Magnéli Ti\textsubscript{4}O\textsubscript{7} (Ru-Ti\textsubscript{4}O\textsubscript{7}) via a straightforward wet impregnation and mild annealing is reported. The Ru-Ti\textsubscript{4}O\textsubscript{7} performs radically active CIER with minimal deployment of Ru (0.13 wt%), both in 5 m NaCl (pH 2.3) and 0.1 m NaCl (pH 6.5) electrolytes. Scanning electrochemical microscopy demonstrates superior CIER selectivity on Ru-Ti\textsubscript{4}O\textsubscript{7} compared to the DSA. 

1. Introduction

Electrolysis of saline water has long been utilized to produce Cl\textsubscript{2} gas or free chlorine species, one of the essential chemicals not only in manufacturing industries as a component of plastics (e.g., polyvinyl chloride) and a bleaching agent, but also in water treatment processes as a disinfectant for ballast water, drinking water, and wastewater.\textsuperscript{[1]} In the latter cases, reactive chlorine species (RCS) play a pivotal role in homogeneous oxidation of aqueous organic and inorganic pollutants. This is because the RCS can avoid mass transfer limitation and extend lifetime in water, as opposed to reactive oxygen species such as \textbullet OH, H\textsubscript{2}O\textsubscript{2}, and O\textsubscript{3}.\textsuperscript{[2]} The majority of the worldwide Cl\textsubscript{2} production (>75 million metric tons yr\textsuperscript{-1}) is handled by chlor-alkali processes with electrochemical chlorine evolution reaction (CIER) in saturated [Cl\textsuperscript{-}] = 6 m NaCl solutions with pH 2 – 4. Dimensionally stable anodes (DSAs), mixed metal oxides (MMOs) based on IrO\textsubscript{2} and RuO\textsubscript{2}, have been predominantly deployed as electrocatalysts.\textsuperscript{[3,4]} Notwithstanding the cutting-edge activity and outstanding durability for wide ranges of pH and [Cl\textsuperscript{-}]), through a direct adsorption of Cl\textsuperscript{-} on Ru\textsuperscript{2+}-O\textsubscript{4} sites as the most plausible pathway, together with stabilized ClO\textsuperscript{*} at low [Cl\textsuperscript{-}] and high pH.
an extended CIER.\textsuperscript{[7–8]} Therefore, SACs coordinated with chemically inert oxide support would be beneficial for long-term stability. To the best of our knowledge, Ru SACs on crystalline metal oxides for the CIER have been explored limitedly. Although recent works with amorphous TiO\textsubscript{2} \textsuperscript{[79]} are intriguing, the Ru anchoring on randomly distributed defect sites could be sensitive to the synthetic condition.

To this end, Ti\textsubscript{3}O\textsubscript{7}, a sub-stoichiometric Magnéli Ti oxide (Ti\textsubscript{n+1}O\textsubscript{n}, 3 ≤ n ≤ 10), has attracted great attention due to its low cost, high electrical conductivity, environmental compatibility, and chemical stability.\textsuperscript{[10]} The oxygen deficiency within shear planes (every 4\textsuperscript{th} layer of TiO\textsubscript{6} octahedra chain) balanced by binary Ti\textsuperscript{4+} and Ti\textsuperscript{3+} induces delocalized d-band electrons and elevated conductivity.\textsuperscript{[11]} The periodically developed oxygen defects within crystalline structure could make the Magnéli Ti\textsubscript{3}O\textsubscript{7}, a promising support for anchoring Ru SACs with a potential magnéliite structure. On the other hand, a surface deactivation by irreversible oxidation of Ti\textsuperscript{4+} upon anodization of Ti\textsubscript{3}O\textsubscript{7} itself could seriously lower the electrochemical conductivity and activity.\textsuperscript{[11]} Thus, Ru doping into defective oxide lattice was expected to maintain the charge carrier density of Ti\textsubscript{3}O\textsubscript{7}.\textsuperscript{[11]}

In order to achieve the aforementioned synergisms, we herein report atomically dispersed Ru-doped Ti\textsubscript{3}O\textsubscript{7} electrocatalysts (Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7}), prepared by a straightforward wet impregnation method with mild annealing. The Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7} catalysts outperform existing DSA materials (Ru\textsubscript{3}−Ti\textsubscript{4}O\textsubscript{7}) in terms of CIER activity (13 mV overpotential at 10 mA cm\textsuperscript{-2} in 5 M NaCl (pH 2.3)). Selectivity is also enhanced for the Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7} catalysts, as demonstrated by both CIER current efficiency (CE) in bulk electrolysis and areal OER activity (13 mV overpotential at 10 mA cm\textsuperscript{-2}). Overpotentials of Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7} were significantly decreased in Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7}-NA (before annealing),\textsuperscript{[14]} as indicated by Ru 3\textit{d}_{5/2} photoelectron spectra (Figure S5a, Supporting Information). These phenomena can be understood by spontaneous oxidation of Ru\textsuperscript{4+} (RuCl\textsubscript{3}) by Ti\textsuperscript{3+} (and partially by air). The atmospheric annealing at 450 °C thereafter generated Ru\textsuperscript{4+} with reduction of Ru\textsuperscript{4+} and Ru\textsuperscript{3+} by Ti\textsuperscript{3+}. Furthermore, the O 1s spectra from oxygen vacancies (O\textsubscript{V}) significantly decreased in Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7} (Figure S6a, Supporting Information) along with the formation of Ru\textsuperscript{4+}. The electron paramagnetic resonance (EPR) signals supported that O\textsubscript{V} sites were occupied and stabilized by Ru cations (Figure S6b, Supporting Information). In comparison, the TiO\textsubscript{n−} layer by coating the Ti-glycolate precursor without Ti\textsubscript{3}O\textsubscript{7} powder showed a small fraction of O\textsubscript{V} which was not altered by the Ru anchoring (Figure S7, Supporting Information), to exclude potential impacts of the TiO\textsubscript{2} layer. Metallic Ru\textsuperscript{4+} was noted only by an extended (24 h) immersion in RuCl\textsubscript{3} (Figure S5a, Supporting Information) with formation of surface nanoparticles (Figure S8, Supporting Information).\textsuperscript{[15]} The Ti 2p spectra\textsuperscript{[16]} of Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7} anode (after annealing at 450 °C) were virtually superimposable to Ti\textsubscript{3}O\textsubscript{7} (Figure S5b, Supporting Information), indicating the thermal energy of the final annealing was primarily consumed for the dynamic perturbation in Ru oxidation states. The oxidation states of Ru were quantitatively assessed by plotting the absorption energy at the first maximum in the first-order derivative of the Ru K-edge X-ray absorption near-edge structure (XANES) pre-edge (Figure 1c).\textsuperscript{[17]} The estimated valency of Ru in Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7} (∼ 2.53) manifests partial reduction of sorbed RuCl\textsubscript{3} to Ru\textsuperscript{4+} without a formation of Ru(0), in accordance with the XPS. On the other hand, the valency state of Ru doped on Ti\textsubscript{3}O\textsubscript{7} (≈ 0.94) by the same method implied greater Ru(0) nanoparticle formation. Accordingly, the inherent and periodic O\textsubscript{V} (dangling O and defects) possessed by Ti\textsubscript{3}O\textsubscript{7} were found to serve as embedding sites for atomic Ru cations with electronic reconstruction by a strong MSI.\textsuperscript{[7,18]} The half-maximum-intensity energy of Ti K-edge XANES spectra displayed that the overall oxidation number of Ti cations substantially decreased due to the wet Ru impregnation, but moderately increased during the final annealing (Figure S9, Supporting Information), which supports the proposed mechanism of a redox-active Ru trapping to Ru\textsubscript{1−}Ti\textsubscript{4}O\textsubscript{7}, mediated by Ti\textsuperscript{3+/4+}.
Figure 1. Preparation and characterization of Ru$_1$-Ti$_4$O$_7$ containing Ru$^{2+}$-O$_4$ sites. a) Schematic representation for Ru$_1$-Ti$_4$O$_7$ preparation via simple wet impregnation and annealing. b) HAADF-STEM image of Ru$_1$-Ti$_4$O$_7$ with line profiles for red dotted boxes in the inset. c) Ru K-edge XANES spectra (estimation of Ru oxidation states in the inset) in parallel with d) $k^3$-weighted Ru K-edge EXAFS spectra of Ru$_1$-Ti$_4$O$_7$ referenced to standards (Ru foil, RuCl$_3$, RuO$_2$) and other specimens (Ru-doped Ti$_5$O$_8$ and DSA). e) Charge density distribution in Ru$_1$-Ti$_4$O$_7$ model (gray for Ti, red for O, and blue for Ru; the cyan and yellow contours indicate electron deficiency and electron accumulation, respectively).
The primary peak at 1.5 Å in the extended X-ray absorption fine structure (EXAFS) spectra of Ru-TiO
2 (Figure 1d) corresponds to Ru-O bonds[19] with coordination number (CN) of 4 (fitted results in Figure S10 and Table S2, Supporting Information). The wavelet transforms (Figure S11, Supporting Information) of the EXAFS spectra further characterized the minor peaks on Ru–Ti–O, beyond the core shell. The peak at ≈3.3 Å in R space could stem from Ru-O-Ru but it was clearly distinct from that of RuO2 (≈2.9 Å) with octahedral geometry, suggesting that the peak originates from neighboring Ru atoms rather than from the aggregation of RuO2. The Ru-Ru peak near 2.4 Å was minute for Ru–TiO
2, but more distinct for Ru-doped TiO
2, again demonstrating that O3 and/or mixed Ti
4+/3+ alleviates metallic Ru formation. The k2-weighted Ti K-edge EXAFS spectrum of Ru–TiO
2 was similar to those of pristine TiO
2 and TiO
2.350, corroborating the formation of Ru
2+O
1- sites on O2 without structural deformation of Ti-O and Ti-Ti bonds (Figure S12, Supporting Information). The integrated crystal orbital Hamilton population (ICOHP) of the Ru-O bond conformed to the stable Ru-O bond formation between Ru SACs and surficial oxygen atoms on TiO
2. The average ICOHP increased with the oxygen coverage (Table S4, Supporting Information), suggesting that the surface of Ru–TiO
2 favors oxygen atoms ab extra. The calculated Ru Bader charge alluded the oxidation state of Ru near 2+ (0.73 e) for Ru in Ru–TiO
2, with 0.25 ML O at open circuit voltage (OCV, Figure S13 and Table S5, Supporting Information). Thus, a dynamic oxidation and reconstruction during the annealing generated stable Ru
2+O
1- sites, in decent agreement with the XAS and XPS characterizations. The charge density difference plot clearly portrayed that the Ru atom strongly binds with the TiO
2 support by MSI, rearranging the interfacial charge distribution by partial electron interchange between Ru and Ti (Figure 1e).[7] The projected density of states (PDOS, Figure S14, Supporting Information) of a theoretical bare Ru-TiO
2 site showed unfavorably sharp free-atom-like Ru d-orbital states below the Fermi energy (E
F), implying a weak interaction with the oxide support.[21] In contrast, the 4d of Ru
2+O
1- sites with 0.25 ML O showed blunt and broadly flattened energy states to indicate stronger orbital hybridization. The valence band XPS (Figure S15, Supporting Information) noted a prominent Ru 4d state near E
F (antibonding interaction with O 2p) for Ru–TiO
2_NA that was significantly alleviated for Ru–TiO
2 after annealing. Concurrently, the intensified Ru 4d bands far below E
F (bonding interaction with O 2p) corroborated stabilized Ru
2+O
1- geometry by O uptake.[22]

These results collectively evinced that our simple and facile impregnation method provides Ru
2+O
1- motifs with minimal use of RuCl3 precursor. The TiO
2 that comprises Ti
4+/3+, Ti
3+, and highly developed and periodical shear plane O
2 in tandem enabled this unique atomic coordination. Considering the ionic electronegativity of Ti (Ti
4+: 1.45, Ti
3+: 1.73) and Ru (Ru
3+: 1.58, Ru
4+: 1.85),[23] the chemical reaction between RuCl3 and TiO
2 could generate Ru
4+ (with Ti
3+ electron acceptor) that was subsequently reduced to Ru
2+ (by Ti
4+ electron donor) during the aerobic thermal treatment.[24] The O3 could assist the Ru
2+O
1- formation with structural flexibility. Upon saturation of the O2 sites on TiO
2, nucleation into metallic Ru nanoclusters occurred as in the case with an extended (24 h) immersion or using TiO
2.[25] The Ru
2+O
1- formation in this study is analogous to the formation mechanism of Pt SAC on CeO
2.[26] Hence, required extensive thermal treatment (e.g., 10 h at 800 °C).

2.2. Electrochemical CIER Performance of Ru–TiO
2

The electrocatalytic activities of the Ru–TiO
2 anode were evaluated in comparison with other Ru-doped TiO
2 anodes analogously prepared with various impregnation durations and precursors (xL or xH where x designates immersion duration (h), while L and H denotes 0.005 and 0.05 m RuCl3 in precursors, respectively). In 5 m NaCl (pH 2.3), the onset of CIER at 10 mA cm
–2 on the Ru–TiO
2, (i.e., 1H) occurred at 1.507 V RHE, corresponding to near-zero overpotential (ƞ) of 13 mV (with IR compensation) based on equilibrium potential of 1.494 V. This ƞ value was far lower than DSA (44 mV) and other Ru–TiO
2 composite anodes (e.g., 21 mV for 24H, Table S6 and Figure S16a, Supporting Information). The normalized voltammograms (Figure 2a) and turnover frequency (TOF, Figure 2b), based on capacitance-based electrochemical active surface area (ECSA, Figure S17, Supporting Information), substantially the intrinsic superior CIER activity of the Ru
2+O
1- motifs on Ru–TiO
2. The CIER TOF and mass activity (Figure S18, Supporting Information), from mass loading measured by inductively coupled plasma mass spectroscopy (ICP-MS, Table S7, Supporting Information), of Ru–TiO
2 were greater than DSA (by 17-fold and 23-fold, respectively, at ƞ of 45 mV). Tafel analysis (Figure 2c) revealed that the CIER on Ru–TiO
2 would proceed via the Volmer-Heyrovsky mechanism as corroborated by a Tafel slope of ≈39 mV dec
–1, that was smaller than 72.81 mV dec
–1 for DSA.[27] The Nyquist plot (Figure S19, Supporting Information) supported far lower charge transfer resistance (R
ct) of Ru–TiO
2 for CIER, compared to 24H and DSA.

In 1 m H2SO4 solutions (pH 0.19), on the other hand, the anodic wave overall diminished substantially (Figure S20, Supporting Information) to indicate more sluggish OER than CIER on Ru–Ti MMOs. The 24H sample with the highest Ru loading marked the minimal OER ƞ. However, Ru–TiO
2 again showed the highest intrinsic OER activity with regard to the ECSA-normalized linear sweep voltammetry (LSV). The Tafel slopes for OER on Ru–TiO
2 (94 – 156 mV dec
–1 depending on ƞ) were apparently greater than DSA (76 – 154 mV dec
–1). These activity trends were reproduced in 0.1 m NaCl with circum-neutral pH (Figure S16b, Supporting Information). This condition corresponds to active chlorine mediated water treatment and allows parallel CIER and OER.

The relatively high current generation of 24H in 0.1 m NaCl would largely be ascribed to OER; the ratio of CIER current (dominating in 5 m NaCl at pH 2.3) to the OER current (in 1 m H2SO4) at a given anodic potential was by far greater for 1H than 24H and DSA (Figure S21, Supporting Information). Figure S22 (Supporting Information) further noted linear relationships of ƞ values at 10 mA cm
–2 (in 5 m or 0.1 m NaCl) with potential of zero charge (PZC), an experimental descriptor for overall surface charge density and propensity toward O adsorption.[28] This observation apparently manifested suitable metal-oxygen bond strength of
Ru-doped Ti4O7 to attenuate both for CIER and OER, compared to DSA.\textsuperscript{[4a]} However, significantly different $\eta$ values depending on electrolyte (particularly for Ru$_1$-Ti$_4$O$_7$ and 24H) intimated potential deviation from the scaling relation, to necessitate elaborated atomic-scale interrogations for unequivocal explanations (vide infra).

The subsequent concern was on the CIER selectivity in terms of CE. The CE values were first evaluated by galvanostatic electrolysis of 5 m NaCl (pH 2.3) and 0.1 m NaCl (pH 6.5) at 20 mA cm$^{-2}$, based on colorimetric quantification of active chlorine in bulk electrolyte (Figure S23, Supporting Information). Comparable CE was observed in 5 m NaCl regardless of the composition of Ru-Ti MMOs, whereas the Ti$_4$O$_7$-350 itself showed a poor CIER selectivity. In 0.1 m NaCl, Ru-doped Ti$_4$O$_7$ samples with comparatively low Ru loadings (1-24L, 1H) showed CE values ($\approx$89%) moderately exceeding the other analogues (12-24H, DSA). The CIER selectivity of Ru$_1$-Ti$_4$O$_7$ (1H) was further assessed in variable combinations of current density ($j$, 10, 20, 50, and 100 mA cm$^{-2}$), pH (2.3, 6.5, 12.0), and [NaCl] (0.1 and 5 m). Figure 2d, e exhibited overall decreasing trends of CE with the increasing $j$ and bulk pH, more clearly in 0.1 m NaCl with a diffusion limitation for Cl$^-$. Varied pH in the anode vicinity and transformations of HOCl to produce ClO$_3^-$ and/or O$_2$ could bias the observed trends.\textsuperscript{[1a]} Nevertheless, the CIER CE of Ru$_1$-Ti$_4$O$_7$ was consistently above 70% under the operational conditions, surpassing the DSA which marked CE value as low as 55% (Figure S24, Supporting Information). The unexpectedly high CEs (78–90%) in pH 12 were noteworthy for Ru$_1$-Ti$_4$O$_7$, suggesting an efficient CIER even in alkaline conditions. Regarding stability, chronopotentiometry (CP) in 5 m NaCl (pH 2.3) at 100 mA cm$^{-2}$ over 100 h demonstrated that Ru$_1$-Ti$_4$O$_7$ could be durable in the harsh environment (Figure 2f). The polarization curve of the used Ru$_1$-Ti$_4$O$_7$ anode was superimposable to the intact one in 5 m NaCl (Figure S25b, Supporting Information). A post-mortem XPS and XANES analysis indicated minimal variations in Ru oxidation state for the used Ru$_1$-Ti$_4$O$_7$ (Figures S25a and S26, Supporting Information).

### 2.3. CIER Selectivity as Unveiled by SECM

The CE estimations by the bulk electrolysis could be biased by a narrow detection limit of the DPD method ($\approx$ 1.4 $\times$ 10$^{-4}$ m Cl$_2$ equivalent), transformations of active chlorine, and variable applied potential in the constant current electrolysis (Figure S23, Supporting Information) because the scaling relation between OER and CIER can be potential dependent.\textsuperscript{[29]} Since these issues have been brought up frequently, the assessment of CIER selectivity has been complemented by kinetic information from Tafel slope or differential electrochemical mass spectrometry (DEMS).\textsuperscript{[30]} However, DEMS necessitates an acidic electrolyte for Cl$_2$ volatilization. In this regard, sample generation/tip collection (SG/TC) mode SECM could precisely distinguish CIER from OER, through the chlorine reduction reaction (CIRR) at the tip, under a wide potential window in near-neutral pH.
Figure 3. Quantification of ClER selectivity of Ru1-Ti4O7 and DSA. Representative CAs of Pt UME tip at 0.393 V (only for ORR) and 0.043 V RHE (for ORR + ClRR) during ClER on a) Ru1-Ti4O7, and b) DSA. The tip current for ClRR (red) was obtained by subtracting ORR current (black) from ORR + ClRR current (blue). c) Estimated CE of ClER on Ru1-Ti4O7 (red) and DSA (black) by means of bulk electrolysis (scatter) and SECM (dotted line) under the step-wise ramping up of $E_S$ (10 mV increment, each for 60 s). Standard deviations were denoted as error bars.

2.4. Active Site and Mechanism of ClER on Ru1-Ti4O7

Figure 4 shows operando XANES analysis of Ru1-Ti4O7. In 0.1 M H2SO4, the Ru K-edge spectra of Ru1-Ti4O7 were superimposable regardless of the applied potentials. In 0.1 M H2SO4 + 1 M NaCl solution, by comparison, the white line intensity noticeably increased along with the ClER at biases above 1.46 V RHE (the equilibrium potential of ClER at pH 0.85). Because these distinct phenomena were not observed in the Ti K-edge spectra (Figure S31, Supporting Information), the noticeable change in Ru oxidation states under the ClER relevant potential range elucidated the single atomic Ru to be the ClER active site. Moreover, the more distinct redox transformation of Ru in the presence of Cl− was reported to evoke a direct Cl− adsorption rather than mediation by ClO−.

First-principles calculations were performed to theoretically evaluate the activity and selectivity of ClER and disentangle the reaction pathways on active motifs of Ru1-Ti4O7. First of all, we determined the most stable surface structure of Ru1-Ti4O7, DSA, and RuO2 (Figure 5a; Figure S32, Supporting Information). In particular, the Ru1-Ti4O7 was featured by Ru atoms attached to the (120) facet of Ti4O7, in agreement with XRD and selected area electron diffraction (SAED) patterns (Figure S3, Supporting Information). Thereafter, surface Pourbaix diagram predicted the most probable oxygen coverage on the Ru1-Ti4O7 surface under variable anodic potential (Figure S33, Supporting Information). It was revealed that coordinately unsaturated sites (CUS) on bare Ru1-Ti4O7 would be increasingly occupied with the oxygen atoms upon the anodic bias, as evidenced by a slight positive shift of the rising Ru K-edge for the used Ru1-Ti4O7 (Figure S26, Supporting Information). While 0.25 ML coverage was preferred in OCV, 0.875 ML O-covered surface was found to be the most probable structure near the onset potentials of ClER and OER. Further, O* attachment was hindered by a substantial energy
requirement for OH* deprotonation to O* (1.39 eV). The Bader charge suggested that the atomic Ru would be progressively oxidized (from 0.94 |e| at 0.25 ML O to 1.57 |e| for 0.875 ML O) upon the potential bias (as references, 1.65 |e| for DSA, and 1.63 |e| for RuO2). In comparison, the Ti Bader charge of Ru1-Ti4O7 (1.85-1.89 |e|) was consistently lower than DSA (1.93 |e|) and TiO2 (1.94 |e|), which corroborates stronger MSI for Ru1-Ti4O7 (FigureS13 and TableS5, Supporting Information).

Among the possible active sites on the Ru1-Ti4O7-0.875 ML O (Figure S34, Supporting Information), Gibbs free energy of Cl adsorption (ΔGCl*) was minimized on Ru CUS, compared to bridge oxygen sites (Ru-O-Ti; s2, s7, and s8) and top oxygen site on Ru (s1). The ΔGCl* for the most stable Ru(CUS)-Cl (1.43 eV for s6) was close to the thermoneutral value (ΔGCl* = 1.36 eV at U = 0 V RHE). Given the ClER on the Ru1-Ti4O7 via Volmer-Heyrovsky pathway as confirmed by Tafel analysis (Figure 2c), the ClER intermediate on Ru CUS could be either Cl* or ClO*, depending on the affinity of O. It is worth noting that the Volmer step (energy barrier of 1.43 eV) would be the potential-determining step (PDS), rather than the Heyrovsky step (energy barrier of 1.29 eV). According to the comprehensive picture on Cl- and ClO-mediated mechanisms with parallel OER (Figure 5b), Figure 5c and 5e illustrate the ClER free energy diagrams on Ru1-Ti4O7(120), in comparison with DSA(110) and RuO2(110). They can be reference with the free energy of OER intermediates in Figure 5d and Table S8 (Supporting Information) (that further summarizes the thermodynamic overpotential (ηTD) and presumed ClER mechanism). The calculated free energy of intermediates shows that direct Cl binding to the Ru CUS of Ru1-Ti4O7 was the most preferable for ClER with an unprecedently low ηTD of 70 mV (Figure 5c), in agreement with the operando XANES (Figure 4). The ΔGCl* was far lower on RuO2 (0.50 eV) and moderately higher on DSA (1.52 eV, equivalent to ηTD of 160 mV) to reduce the ClER activity in line with Sabatier’s principle. The PDOS and projected crystal Hamilton population (pCOHP) analysis on adsorbed Cl could comparatively unravel the bond strength of Ru-Cl* that in-turn depends on the populations of bonding and antibonding states below E (Figure S35, Supporting Information). The overlapping of Cl 3p and Ru 4d orbital near E (0 > -pCOHP, antibonding) for Ru1-Ti4O7 exceeded the pairwise interaction area below -1.5 eV (0 < -pCOHP, bonding), to indicate more favorable Cl desorption and facilitated ClER than RuO2. Figure S36 (Supporting Information) further shows that relatively concentrated electrons of Ru 4d(z2) states in Ru1-Ti4O7 contributed to the ClER-friendly state of Ru-Cl* bond, compared to the electrons dispersed in three directions of Ru 4d(x2-y2), 4d(xz), 4d(yz) states of RuO2.

Moreover, Figure 5e shows that the ClER on Ru1-Ti4O7(120) could also be mediated by chemisorbed O* on Ru CUS (s6 in Figure S34, Supporting Information) with slightly greater ηTD of 80 mV compared to that for the Cl-mediated mechanism (ηTD of 70 mV). Though the O* formation energy on Ru CUS of RuO2(110) was lower than that of Ru1-Ti4O7(120), subsequent discharge of Cl* and ClO* formation necessitated prohibitively high energy (1.81 eV) to increment ηTD (450 mV). On the other hand, O* formation on the DSA surface required 2.28 eV, ruling out OER-mechanism on our DSA model; even on presumed O* at a sufficiently high potential, cleavage of ClO* intermediate (Heyrovsky step) would limit the ClER (ηTD = 300 mV). Accordingly, the ClO-mechanism for DSA and ClO-mechanism for RuO2 would be the plausible scenarios (Table S8, Supporting Information), in agreement with the prior theoretical studies.[33] Strikingly, both Cl* and ClO* intermediates could be adequately stabilized on Ru1-Ti4O7, with near-zero ClER overpotentials (ηTD: 70 – 80 mV) irrespective of the ClER pathways. For the competing heterogeneous OER, the OH* deprotonation step was found to be the PDS of Ru1-Ti4O7 with thermodynamic energy barrier of 1.62 eV (ηTD = 390 mV). This value was lower than the energy constraint for PDS on DSA (OH* deprotonation, 2.28 eV) and on RuO2 (OOH* formation, 1.96 eV), to confirm superior OER activity on Ru1-Ti4O7 as substantiated experimentally (Figure S20, Supporting Information). Because the bound O* could mediate ClER and OER simultaneously,[44] a scaling relation between ClO* and OH* has oftentimes described the selectivity.[4c] Our calculations also revealed a linear free energy relationship between ClO* and OOH* (Table S8, Supporting Information) on the models.

**Figure 4.** Identification of ClER active site on Ru1-Ti4O7. Operando Ru K-edge XANES spectra of Ru1-Ti4O7 a) in the absence (0.1 m H2SO4, pH 1.05) and b) the presence of Cl− (0.1 m H2SO4 + 1 m NaCl, pH 0.85). Applied potential was sequentially incremented from OCV to 1.67 V RHE. The inset figures display how the absorption intensity changes with applied potentials at specific energy level (E1) of the white line.
Figure 5. Gibbs free energy diagrams for CIER and OER mechanisms on constructed Ru$_{1}$-Ti$_{4}$O$_{7}$, DSA, and RuO$_{2}$ model. DFT-optimized structures of a) Ru$_{1}$-Ti$_{4}$O$_{7}$(120), Ru$_{0.3}$Ti$_{0.7}$O$_{2}$(110), and RuO$_{2}$(110). b) Possible CIER and OER mechanisms on Ru-Ti oxide surface. Gibbs free energy diagrams of c) CIER through Cl-mechanism, d) OER, and e) CIER through ClO-mechanism.
under interrogation (RuTiOx, DSA, and RuO2), with more sluggish OER than CIER. It is rational to postulate that the direct Cl\(^-\) chemisorption would be preferred in chloride-rich conditions (e.g., 5 m NaCl) to break the scaling relation, which would improve the CIER selectivity in chlor-alkali processes. As [Cl\(^-\)] decreases and pH increases (as in water treatment processes), the ClO* formation could be facilitated to mediate CIER. Consequently, the parallelly active Cl- and ClO-mechanisms on the Ru\(_{1}\)-TiO\(_7\) electrodes support, ultimately to enhance the activity and selectivity of the ClER performance even in low [Cl\(^-\)] and pH.

3. Conclusion

In this study, Ru SAC periodically anchored on crystalline metal oxide (Magnéli Ti\(_3\)O\(_7\)) was synthesized as Ru\(_{1}\)-TiO\(_7\) comprising Ru\(_{2}\)-O\(_2\) active sites for highly efficient CIER. A simple wet impregnation and atmosphericannealing allowed Ru atom trapping on TiO\(_2\) by inherent redox active Ti\(^{1+}/4+\) and O\(_2\). The Ru\(_{1}\)-TiO\(_7\) (0.13 wt% of Ru) exhibited outstanding activity and selectivity toward CIER, to complement existing DSA. Notably, SEC quantitatively demonstrated superior CIER selectivity under a wide potential range in near-neutral pH. The operando XANES and DFT calculations corroborated that the ClER on Ru\(_{1}\)-TiO\(_7\) was primarily mediated by a direct Cl\(^-\) adsorption on Ru\(_{2}\)-O\(_2\) active sites, to escape the scaling relation between OOH* and ClO*. A proper ClO* formation energy synergistically contributes to the CIER performance even in low [Cl\(^-\)] and/or circum-neutral pH, to allow universally active and selective CIER. The innovative findings of this study raise broad implications on SACs on metal oxide supports, ultimately to enhance the activity and selectivity of variable electrochemical redox reactions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cloration evolution reaction, electrocatalysis, Magnéli Ti\(_3\)O\(_7\), scanning electrochemical microscopy, single-atom catalysts


